

Nutrient uptake in streams draining agricultural catchments of the midwestern United States

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SUMMARY

1. Agriculture is a major contributor of non-point source pollution to surface waters in the midwestern United States, resulting in eutrophication of freshwater aquatic ecosystems and development of hypoxia in the Gulf of Mexico. Agriculturally influenced streams are diverse in morphology and have variable nutrient concentrations. Understanding how nutrients are transformed and retained within agricultural streams may aid in mitigating increased nutrient export to downstream ecosystems.

2. We studied six agriculturally influenced streams in Indiana and Michigan to develop a more comprehensive understanding of the factors controlling nutrient retention and export in agricultural streams using nutrient addition and isotopic tracer studies.

3. Metrics of nutrient uptake indicated that nitrate uptake was saturated in these streams whereas ammonium and phosphorus uptake increased with higher concentrations. Phosphorus uptake was likely approaching saturation as evidenced by decreasing uptake velocities with concentration; ammonium uptake velocity also declined with concentration, though not significantly.

4. Higher whole-stream uptake rates of phosphorus and ammonium were associated with the observed presence of stream autotrophs (e.g. algae and macrophytes). However, there was no significant relationship between measures of nutrient uptake and stream metabolism. Water-column nutrient concentrations were positively correlated with gross primary production but not community respiration.

5. Overall, nutrient uptake and metabolism were affected by nutrient concentrations in these agriculturally influenced streams. Biological uptake of ammonium and phosphorus was not saturated, although nitrate uptake did appear to be saturated in these ecosystems. Biological activity in agriculturally influenced streams is higher relative to more pristine streams and this increased biological activity likely influences nutrient retention and transport to downstream ecosystems.

Keywords: agriculture, nitrogen, nutrient uptake, phosphorus, stream

Introduction

Agricultural activities influence aquatic ecosystems by increasing nutrient inputs, which can result in changes to both ecosystem structure and function

(Howarth *et al.*, 1996; Vitousek *et al.*, 1997; Tilman *et al.*, 2003). In-stream concentrations and catchment export of nitrogen (N) and phosphorus (P) tend to increase with increasing agricultural land use in a catchment (e.g. Mason *et al.*, 1990; Correl, Jordan & Weller, 1992; Baker & Richards, 2003; Nord & Lanyon, 2003). The effects of increased nutrients on freshwater and marine ecosystems are well documented and include eutrophication (Downing *et al.*, 1999), hypoxia

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(Rabalais, Turner & Wiseman, 2002) and decreased biodiversity (Vitousek *et al.*, 1997). Additionally, elevated nitrate (NO_3^- -N) concentrations in drinking water have been associated with human health risks, such as methyhemoglobinemia and non-Hodgkin's lymphoma (USEPA, 1990; Townsend *et al.*, 2003).

Recent advances in our understanding of nutrient uptake and transformation in streams are almost exclusively based on studies of small streams in relatively undisturbed ecosystems (i.e. Marti, Grimm & Fisher, 1997; Mulholland *et al.*, 2000; Tank *et al.*, 2000; Peterson *et al.*, 2001; Wollheim *et al.*, 2001; Hall & Tank, 2003). Most of these streams have low nutrient concentrations and many are heavily shaded with low autotrophic production (except see Grimm & Fisher, 1986; Marti *et al.*, 1997; Dodds *et al.*, 2000). Streams in relatively undisturbed ecosystems differ substantially from those found in agricultural regions, such as the midwestern United States. Nutrient concentrations in catchments with high agricultural activity can be orders of magnitude higher than undisturbed catchments (e.g. Kemp & Dodds, 2001, 2002a,b; Vanni *et al.*, 2001; Royer, Tank & David, 2004; Inwood, Tank & Bernot, 2005) and most agricultural streams have reduced riparian vegetation resulting in an open canopy and increased primary production. Additionally, agricultural catchments in the midwestern United States are often artificially drained with subterranean tiles that lower the water table and maintain unsaturated soils for farming. In tile-drained catchments, water and dissolved nutrients are discharged rapidly to stream channels, bypassing riparian flowpaths and thereby reducing the opportunity for nutrient uptake and retention that could occur in these areas (e.g. Peterjohn & Correl, 1984).

To effectively manage nutrients in agricultural streams, a greater understanding is needed of how nutrients are processed within these highly modified systems. Whereas hydrology is known to be important in controlling nutrient export from agricultural catchments, biotic retention of nutrients in agriculturally influenced streams has not been studied. Hydrology often controls the timing and magnitude of nutrient inputs to streams (David & Gentry, 2000; Kemp & Dodds, 2001; Petry *et al.*, 2002) and hydrological modifications, such as tile-drains, may limit biotic uptake of nutrients in agricultural streams if the modifications reduce the residence time of the water (Jansson *et al.*, 1994; Royer *et al.*, 2004). For example,

biological uptake of nutrients is expected to plateau as a stream becomes nutrient saturated (Davis & Minshall, 1999), but this expectation has not been examined in nutrient-rich and highly productive agricultural streams.

Our goal was to quantify nutrient uptake rates and examine controls on nutrient retention in relation to nutrient concentrations and ecosystem metabolism in a set of streams draining agricultural catchments. Specifically, we asked whether agricultural streams displayed the expected pattern of nutrient saturation (after Davis & Minshall, 1999; Bernot & Dodds, 2005). The predicted theoretical relationship between nutrient concentration and nutrient uptake (U) indicates that as nutrient concentration increases, U will become saturated (Davis & Minshall, 1999). Furthermore, as U approaches saturation, uptake velocity (v_f) will decrease rapidly due to decreased demand. Thus, calculation of multiple metrics of nutrient uptake (i.e. S_w , U , v_f) enhances our understanding of nutrient processing within the stream. Additionally, we examined the relationship between nutrient uptake and stream channel complexity by relating transient storage and nutrient retention in agricultural streams. Finally, we compare our results from nutrient-rich agricultural streams with previously published work from less disturbed streams to assess the effects of agricultural activity on in-stream nutrient uptake.

Methods

Site descriptions

We selected six sites for analysis of nutrient retention and uptake rates (Table 1). Five sites were located in the Kalamazoo River catchment in southwest Michigan and one site in the Iroquois-Kankakee catchment in northwestern Indiana. Sites were selected based on stream size, drainage area and per cent of catchment in row-crop agriculture (Table 1). We quantified agricultural landuse in the surrounding catchment using geographic information system (GIS) data layers. Internet-accessible GIS databases were used to obtain images (1997–2000 LANDSAT Thematic Mapper) and data layers were subsequently combined using ArcGIS (Environmental Systems Research Institute, Inc., 2002). All sites had 50% or greater of the total drainage area in row-crop agriculture.

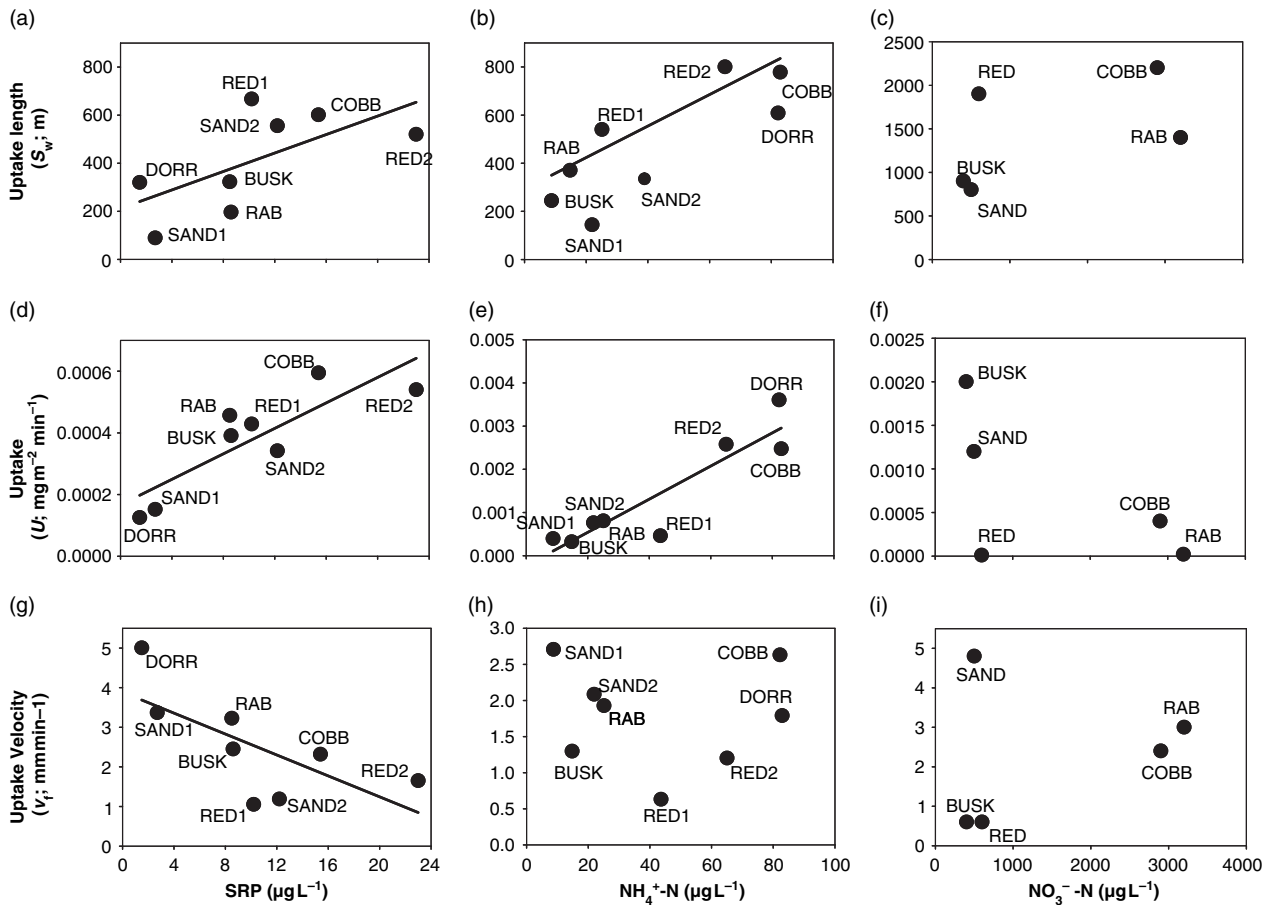


Fig. 1 Relationships between nutrient concentration and nutrient uptake length (S_w), uptake velocity (v_t) and uptake rate (U) in agriculturally influenced streams. Nutrient concentrations are those at the time of uptake measurements. Lines represent linear regressions; see text for regression statistics and Table 1 for site abbreviations. Numbers following site abbreviations denote sites where more than one measurement was made.

Table 1 Site abbreviations and catchment characteristics for agricultural streams in this study

Site	Abbreviation	State	Catchment	Coordinates	Stream order	Drainage area (km ²)	Per cent agricultural landuse
Buskirk Drain	BUSK	MI	Kalamazoo	42°38'09"N, 85°39'44"W	1	0.6	91
Tributary to Sand Creek	SAND	MI	Kalamazoo	42°34'42"N, 85°55'42"W	1	0.8	50
Red Run Drain	RED	MI	Kalamazoo	42°42'28"N, 85°41'31"W	1	1.1	93
Little Rabbit River	RAB	MI	Kalamazoo	42°46'21"N, 85°32'39"W	1	5.4	79
Urban Drain (City of Dorr, MI)	DORR	MI	Kalamazoo	42°43'39"N, 85°43'17"W	2	15.0	65
Cobb Ditch	COBB	IN	Iroquois-Kanakakee	41°02'14"N, 87°02'02"W	3	77.7	90

Drainage areas were then estimated according to elevation data and ground observations. Discharge data were compiled using available US Geological Survey real-time data developed from stage-flow regressions.

Physiochemical characteristics

We collected filtered (Gelman A/E (Pall Gelman Sciences, East Hills, NY, U.S.A.), 0.45 μ m nominal pore size) water samples from the stream thalweg into

acid-washed, stream-rinsed Nalgene bottles for nutrient analyses. All samples were placed on ice, transported to the laboratory and frozen for later analyses. Water samples were analysed for soluble reactive phosphorus (SRP; modified molybdenum blue ascorbic acid method, APHA, 1995), nitrate (NO_3^- -N; Dionex ion chromatograph; modified USEPA Method 300.0, 1993), ammonium (NH_4^+ -N; phenol-hypochlorate spectrophotometric analysis, Solorzano, 1969) and dissolved organic carbon (DOC; Shimadzu 5000A carbon analyzer for total non-purgeable organic content from acidified water samples, APHA, 1995). Minimum detection limits for samples collected were: SRP = $5 \mu\text{g L}^{-1}$, NO_3^- -N = $5 \mu\text{g L}^{-1}$, NH_4^+ -N = $0.5 \mu\text{g L}^{-1}$. Instantaneous measurements of stream temperature, dissolved oxygen (in mg L^{-1} and per cent saturation), conductivity ($\mu\text{S cm}^{-1}$) and pH were made with a Hydrolab[®] minisonde (Hach Environmental, Loveland, CO, U.S.A.).

Nutrient uptake

Measurements of nutrient uptake via short-term nutrient additions, transient storage, whole-reach metabolism (six streams in 2002 and two streams in 2003) and ^{15}N tracer isotope additions (five streams in 2002) were collected during baseflow conditions. We measured nutrient uptake in streams using short-term (1–3 h) additions of NH_4^+ -N and SRP (in conjunction with Br^- as a conservative tracer) as described previously (Stream Solute Workshop, 1990). These data were used to calculate NH_4^+ -N and SRP uptake length (S_w), uptake velocity (v_t) and uptake rate (U).

Additions were conducted by collecting background filtered water samples at six to 10 stations along a stream reach ranging from 200 to 500 m in length (depending on discharge and background nutrient concentration) and adding a concentrated solution of ammonium chloride (NH_4Cl) or potassium phosphate (KH_2PO_4) with sodium bromide (NaBr) into the stream for approximately 2 h with a peristaltic pump until concentrations were stable through time at the most downstream station. Plateau samples were then collected in triplicate at each of the designated stations. Samples were stored on ice and analysed within 48 h or frozen for later analysis of NH_4^+ -N and SRP as previously described. Mean nutrient concentrations in each sample were divided

by bromide (Br^-) concentrations (analysed in conjunction with NO_3^- -N on ion chromatograph) to correct for nutrient decreases caused by downstream increases in discharge rather than nutrient uptake. Nutrient uptake lengths (in m; S_w) were calculated as the inverse of significant slopes ($P < 0.1$) obtained by regressing $\ln(\text{tracer nutrient/tracer bromide})$ versus distance downstream from release site (Stream Solute Workshop, 1990). Uptake velocity (v_t) and uptake rate (U) were also calculated using stream nutrient concentrations and discharge (Stream Solute Workshop, 1990).

In five streams (RAB, COBB, RED, SAND, BUSK; see Table 1 for site description), NO_3^- -N uptake length was measured using short-term ^{15}N tracer additions. K^{15}NO_3 was added to the stream for 2–3 h to reach a target enrichment of 20 000 per mil $\delta^{15}\text{N}$ to allow for ^{15}N tracer incorporation into biomass compartments via NO_3^- -N uptake. Following the 2 to 3 h addition, samples were collected for ^{15}N analysis along a 200 m reach from high turnover compartments including filamentous green algae, bacterial biofilms and macrophytes. Collected samples were dried, ground and then analysed by mass spectrometry at the UC Davis Isotope Laboratory. Nitrate uptake length was then calculated using the inverse of the slope of the regression of $\ln(\delta^{15}\text{N}$ in biomass) over distance similar to the calculation for short-term nutrient addition uptake lengths described above (Tank, Bernot & Rosi-Marshall, in press).

Transient storage

Transient storage was estimated by fitting a one-dimensional solute transport model to the pattern of Br^- concentration over time during the short-term nutrient additions (Bencala & Walters, 1983; Runkel, 1998). Water samples for Br^- concentrations were collected at one downstream station every 30 s, for rising and falling concentration periods, and every 5 min during the plateau period (Webster & Ehrman, 1996). OTIS-P, the one-dimensional transport with inflow and storage model developed by Runkel (1998), was parameterised to fit the Br^- data. This model is a modified version of the original OTIS that couples the solution of the governing equation with a non-linear regression package, thereby automating the parameter estimation process (Runkel, 1998).

Whole-reach metabolism

Metabolism was estimated during baseflow in five streams in 2002 by measuring oxygen concentrations at 10 min intervals at the top and bottom of each study reach using Hydrolab[®] minisondes. We calculated whole-reach metabolism as the difference in interval oxygen concentrations (upstream versus downstream) while accounting for the re-aeration of oxygen with the atmosphere (Odum, 1956; Marzolf, Mulholland & Steinman, 1994; modified by Young & Huryn, 1998). Discharge changed <5% over the reach for all streams, and thus, no corrections for groundwater input were made. By integrating these oxygen measurements during a continuous 36 h period, estimates of community respiration and gross primary production rates were calculated. The re-aeration coefficient was calculated by adding propane and regressing the decrease in bromide-corrected propane concentrations over the distance of the reach as described for nutrient uptake lengths above (Wanninkhof, Mulholland & Elwood, 1990). Propane concentrations were measured using gas chromatography.

Calculations and statistics

Linear regression was used to relate nutrient uptake, metabolism and transient storage to site descriptors including NO₃⁻-N, NH₄⁺-N and SRP concentrations. Repeated measures ANOVA was used to measure differences between concentrations and export (calculated as discharge multiplied by concentration) of nutrients among different streams and nutrient types. All statistical analyses were performed using SAS

(System for Windows V8; SAS Institute, Inc., Cary, NC, USA).

Results

Overall, water-column NO₃⁻-N concentrations were highest, followed by DOC, SRP and NH₄⁺-N concentrations, respectively, at all sites (Table 2). One stream (RED) repeatedly had the highest concentrations of NH₄⁺-N, SRP and DOC concentrations, whereas another stream (RAB) had the highest NO₃⁻-N concentrations (Tables 1 and 2). Ammonium and SRP concentrations were, on average, more variable within each site than NO₃⁻-N and DOC concentrations, based on the higher per cent coefficient of variation (Table 2). Discharge was the most variable parameter measured (Table 2) and mean annual discharge was correlated with drainage area ($R^2 = 0.92$, $P < 0.01$; data not shown).

Nutrient uptake

In these agriculturally influenced streams, mean SRP uptake length (S_w) was shorter than NH₄⁺-N S_w , followed by NO₃⁻-N S_w , which was longest (Fig. 1a–c). Mean uptake (U) of NH₄⁺-N was greater than U of NO₃⁻-N and SRP respectively (Fig. 1d–f), whereas, NH₄⁺-N uptake velocity (v_f) was low relative to NO₃⁻-N and SRP v_f respectively (Fig. 1g–i).

Ammonium-N and SRP uptake lengths were positively correlated with respective nutrient concentrations (NH₄⁺-N, $R^2 = 0.34$, $P = 0.002$; SRP, $R^2 = 0.054$, $P < 0.001$). Nitrate-N concentration did not correlate with any measure of nutrient uptake (Fig. 1c,f,i).

Table 2 Discharge and water-column nutrient concentrations from 2002 sampling streams of the midwestern United States influenced by agricultural activity

Site	<i>n</i>	<i>Q</i> (L s) ⁻¹	NH ₄ ⁺ -N (µg L ⁻¹)	NO ₃ ⁻ -N (mg L ⁻¹)	SRP (µg L ⁻¹)	DOC (mg L ⁻¹)
BUSK	8	1.5 (0–7; 175)	12 (9–14; 18)	4.3 (3.2–6.1; 33)	11 (2–23; 70)	5.7 (0–9; 34)
SAND	12	7 (0.1–25.8; 104)	28 (6.6–83; 80)	0.2 (<0.01–0.4; 49)	6.2 (2–11.8; 52)	4.3 (2–7; 38)
RED	8	17 (0–53; 118)	144 (25–179; 117)	2.4 (0.8–4.1; 44)	262 (73–664; 106)	16.8 (11–24; 25)
RAB	12	63 (16–153; 74)	40 (3–143; 93)	5.1 (2.7–6.7; 23)	11 (3–28; 72)	4.8 (2–10; 55)
COBB	13	575 (96–2067; 160)	33 (31–197; 40)	4.7 (2.6–6.2; 90)	53 (3–599; 240)	6.2 (3–9; 69)

Values = annual mean (range; per cent variation). All discharge per cent variation calculated using US Geological Survey daily average discharge ($n = 365$). DORR was not measured for monthly physiochemical characteristics. Variation in the number of samples is due to some sites not always having flowing water during the time of monthly sampling.

BUSK, Buskirk Drain; SAND, Tributary to Sand Creek; RED, Red Run Drain; RAB, Little Rabbit River; COBB, Cobb Ditch; DORR, Urban Drain (City of Dorr, MI); SRP, soluble reactive phosphorus; DOC, dissolved organic carbon.

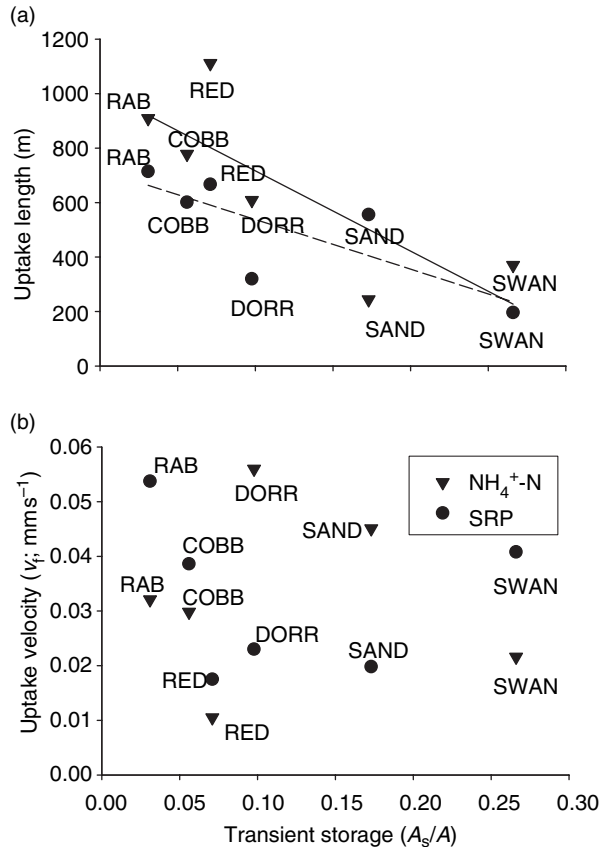


Fig. 2 Relationships between transient storage (A_s/A) and $\text{NH}_4^+\text{-N}$ and SRP (a) uptake length (S_w) and (b) uptake velocity (v_f). Lines represent significant linear regressions; see text for regression statistics.

$\text{NH}_4^+\text{-N}$ and SRP S_w and U were positively related to water-column $\text{NH}_4^+\text{-N}$ and SRP concentrations respectively ($\text{NH}_4^+\text{-N}$, $R^2 = 0.82$, $P = 0.001$; SRP, $R^2 = 0.50$, $P < 0.001$; Fig. 1b,e). There was no relationship between $\text{NH}_4^+\text{-N}$ concentration and $\text{NH}_4^+\text{-N}$ v_f (Fig. 1h), but SRP concentration was negatively related to SRP v_f ($R^2 = 0.59$, $P < 0.001$; Fig. 1g), consistent with potential SRP uptake saturation. Ammonium v_f generally declined with increasing $\text{NH}_4^+\text{-N}$ concentration, although two sites with high concentrations had higher v_f (DORR, COBB; Fig. 1h) yielding no significant relationship when all sites were combined.

Transient storage

Overall, the cross-sectional area of the storage zone (A_s) relative to the cross-sectional area of the stream channel (A) was low at all study sites (Fig. 2). The ratio A_s/A was negatively correlated with both $\text{NH}_4^+\text{-N}$

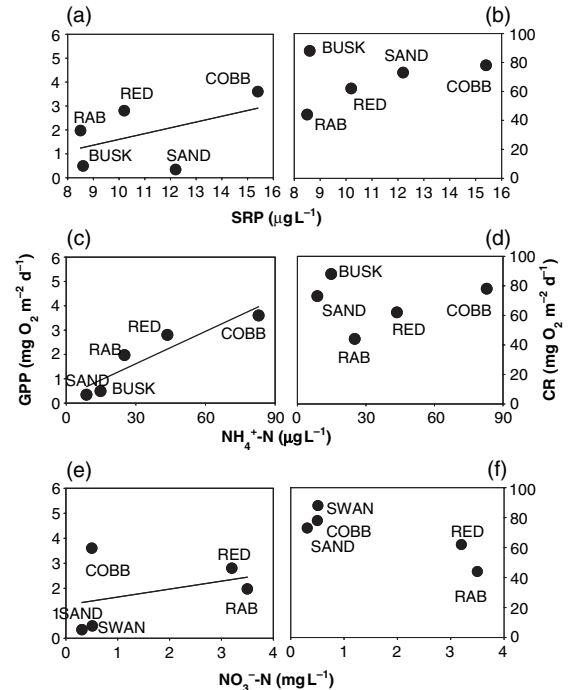


Fig. 3 Relationship between water-column nutrient concentrations and whole-reach gross primary production (GPP; panels a,c,e) and community respiration (CR; panels b,d,f). Nutrient concentrations are those at the time of metabolism measurements. Lines represent significant linear regressions; see text for regression statistics.

N and SRP S_w but not v_f (Fig. 2a). Other hydrological variables including stream discharge, dispersion or storage areas alone were not significantly related to measures of nutrient uptake ($P > 0.1$; data not shown).

Stream metabolism

Gross primary production was significantly positively related to water-column $\text{NO}_3^-\text{-N}$, $\text{NH}_4^+\text{-N}$ and SRP concentrations (Fig. 3a,c,e), with the strongest relationship between $\text{NH}_4^+\text{-N}$ concentrations and gross primary production indicating that water-column nutrient concentrations likely influence stream metabolism. There was no relationship between water-column nutrient concentrations and community respiration (Fig. 3b,d,f). Thus, the biological response to nutrient concentrations was primarily by autotrophs, not heterotrophs, in these high nutrient agricultural streams. There was no significant relationship ($P > 0.1$) between nutrient uptake parameters and gross primary production or community respiration (data not shown) likely due to the

multiple controls on gross estimates of whole-stream metabolism (i.e. light, temperature, pH as well as nutrient uptake).

Discussion

In contrast to previous studies, the per cent of agriculture in the surrounding catchment of these streams was not correlated with NO_3^- -N, NH_4^+ -N, SRP or DOC concentrations (data not shown). However, Jordan, Correl & Weller (1997) found that concentrations of N species increased as the proportion of cropland increased (40–90%). This inconsistency may be due to the selection of our study streams. All sites were selected for high agricultural intensity in the surrounding catchment (Table 1), with all sites having >50% of the catchment in row-crop agriculture (primarily corn and soybean). A broader range of agricultural activity within the catchment may have resulted in this variable being a good predictor of nutrient concentrations. The lack of a significant correlation in our study streams indicates that there may be a threshold value where increases in the percentage of the catchment in agriculture no longer influences stream nutrient concentrations.

We used two different methods to quantify nutrient uptake parameters in these agriculturally influenced streams: nutrient enrichment releases (NH_4^+ -N and SRP uptake) and ^{15}N isotope releases (NO_3^- -N uptake). Because these streams have high nutrient concentrations (Table 2) the methods are comparable. For example, if NO_3^- -N concentrations were low, nutrient enrichment methods for determining uptake would likely yield higher estimates of nutrient uptake, relative to isotopic methods, due to stimulation of uptake (Dodds *et al.*, 2002; Webster *et al.*, 2003; Payn *et al.*, 2005). Because isotopic experiments are expensive and radioactive in the case of phosphorus, we were unable to conduct isotopic experiments for all nutrient forms. We chose to conduct isotopic releases specifically for NO_3^- -N because of the concerns regarding NO_3^- -N loading in agriculturally influenced streams.

We predicted that these high-nutrient, agriculturally influenced, streams would exhibit characteristics of uptake saturation based on Michaelis–Menten kinetics (e.g. Davis & Minshall, 1999; Kemp & Dodds, 2002a,b). Furthermore, in conjunction with saturation of U , v_f would decrease due to the lower demand for

nutrients (Davis & Minshall, 1999). At all sites, NO_3^- -N concentrations and export were greatest followed by NH_4^+ -N and SRP respectively (data not shown). Consistent with higher concentrations and export, biotic uptake of NO_3^- -N (U) was not higher at greater concentrations (Fig. 1f). However, NH_4^+ -N and SRP U were higher at greater concentrations (Fig. 1d,e). Both NH_4^+ -N and SRP U were likely approaching biotic saturation because as NH_4^+ -N and SRP U increased, v_f declined (Fig. 1g,h), due to decreased demand as predicted with uptake saturation (Davis & Minshall, 1999). Nitrate U may have been at saturation at the lowest NO_3^- -N concentrations observed in this study, as there was also a general decline in v_f for NO_3^- -N at the higher concentrations (Fig. 1i). Overall, the greatest ecosystem demand was for SRP, as evidenced by the highest mean v_f , followed by NH_4^+ -N and NO_3^- -N which were not significantly different from each other.

Because v_f is a measure of nutrient uptake independent of stream size and discharge, comparing values across ecosystems is particularly useful. In this study, NO_3^- -N v_f ranged from 0.6 to 4.8 mm min^{-1} (Fig. 1), demonstrating higher ecosystem demand for NO_3^- -N than in forested mountain streams where NO_3^- -N v_f ranged from 0 to 1.6 mm min^{-1} (Bernhardt, Hall & Likens, 2002). In contrast, demand for NO_3^- -N in the agriculturally influenced streams of this study was in the same range as demand in relatively pristine intermountain sagebrush streams (NO_3^- -N $v_f = 0$ –9 mm min^{-1} ; Hall & Tank, 2003). Both NH_4^+ -N and SRP v_f (0.6–2.7 and 1.14–4.92 mm min^{-1} respectively; Fig. 1) were low relative to previous studies in forested mountain streams (NH_4^+ -N $v_f = 0.8$ –8.29 mm min^{-1} , PO_4 $v_f = 0.9$ –11.6 mm min^{-1} ; Hall, Bernhardt & Likens, 2002), intermountain sagebrush streams (NH_4^+ -N $v_f = 1.1$ –12.6 mm min^{-1} ; Hall & Tank, 2003) and in relatively pristine streams across North America as observed in an interbiome study (NH_4^+ -N $v_f = 0.6$ –47 mm min^{-1} ; Webster *et al.*, 2003).

Agriculturally influenced streams are designed to quickly move water away from the land. Thus, transient storage in these systems is low relative to other ecosystems (Runkel, 1998; Webster *et al.*, 2003). Despite low transient storage, NH_4^+ -N and SRP S_w decreased with higher transient storage (Fig. 2a). However, S_w is correlated with higher discharge, yielding longer S_w (Stream Solute Workshop, 1990) and transient storage is negatively correlated with

discharge (Runkel, 1998). Thus, based on discharge alone, we would expect a negative relationship between transient storage and S_w as observed (Fig. 2a). If biological uptake were influenced by changes in transient storage, we would expect an increase in v_f with higher transient storage, which was not observed (Fig. 2b). A previous study in relatively pristine streams with little geographical variation and a larger range in transient storage showed that transient storage could account for only 14–35% of the variation in $\text{NH}_4^+\text{-N}$ v_f but none of the variation in SRP v_f (Hall *et al.*, 2002). In contrast, our data indicate that transient storage does not relate to biological uptake of $\text{NH}_4^+\text{-N}$, potentially due to the low transient storage overall, the low variability in transient storage or the large geographical region, which may be more influenced by variables such as precipitation patterns or geology. Higher transient storage is likely to increase nutrient uptake in low nutrient streams due to higher retention times of nutrients. Because the streams in this study were nutrient-rich agricultural streams, demand for nutrients by organisms (measured as v_f) was not limited by the retention of those nutrients.

Streamwater NO_3^- -N, NH_4^+ -N and SRP concentrations were positively related to gross primary production but not community respiration (Fig. 3) with higher primary production in the presence of higher nutrient concentrations. This indicates that increased nutrients associated with agricultural activities are primarily stimulating autotrophs, not heterotrophs, consistent with increased U with increased nutrient concentrations (Fig. 1) and field observations of large periphyton communities. Heterotrophs may be more influenced by factors such as benthic organic matter quality and the presence of oxygen in the stream benthos, which were not measured in this study. Alternatively, gross primary production estimates are generally more robust than community respiration estimates as small errors in re-aeration and groundwater input measures may have a substantial influence on community respiration estimates (McCutchan *et al.*, 2003; Hall & Tank, 2005). Overall, nutrient concentrations in this study explained 50–90% of the variation in gross primary production, similar to relatively pristine streams where nutrient concentrations explained 75–80% of the variation in gross primary production (Hall & Tank, 2003). Consistent

with higher $\text{NH}_4^+\text{-N}$ U (Fig. 1), relative to SRP and NO_3^- -N U , the strongest relationship was between $\text{NH}_4^+\text{-N}$ concentration and gross primary production (Fig. 2a). In addition to relatively high concentrations of nutrients in our study streams, there was little riparian cover and ample light, allowing for proliferation of autotrophs. Additionally, more frequent scouring of periphyton in agricultural streams, due to channel dredging, tile flow and frequent high flows, may have caused increased biotic uptake by constant new growth of periphyton (Marti *et al.*, 1997). Nutrients have previously been found limiting at high ambient concentrations when large algal mats are present and limiting conditions ensue inside the algal mats due to diffusion limitations (Bushong & Bachmann, 1989). This is one mechanism potentially yielding the $\text{NH}_4^+\text{-N}$ and SRP limitations observed in this study (Fig. 1).

Conclusion

Overall, concentrations of NO_3^- -N, NH_4^+ -N and SRP in this study were 10 times greater than measurements from relatively pristine systems (Table 2; e.g. Hamilton *et al.*, 2001; Kemp & Dodds, 2001; Boyer *et al.*, 2002; Hall & Tank, 2003; Webster *et al.*, 2003). The combined effect of fertiliser use, fixation in crop lands and soil disturbance makes agriculture the largest overall source of nutrients to lotic ecosystems and this fact continues to generate concerns that the ecological integrity and environmental health of terrestrial, freshwater and coastal marine ecosystems are now at risk. We found that biological processes of nutrient uptake and metabolism were affected by nutrient concentrations in nutrient-rich agriculturally influenced streams. Biological uptake was not saturated, as evidenced by increased uptake with higher concentrations of $\text{NH}_4^+\text{-N}$ and SRP and high demand for SRP (Fig. 1). However, nitrate uptake did appear to be saturated in these ecosystems. Additionally, transient storage did not influence biotic activity within these streams potentially due to the low transient storage overall and high nutrient concentrations, which decreased the need for retention mechanisms (Fig. 2). Transient storage is likely controlled primarily by abiotic factors including hydrology, soils and climate. Our study demonstrates that biological activity in agriculturally influenced streams is high relative to more pristine streams and this increased biological

activity likely influences nutrient retention and transport to downstream ecosystems.

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References

- APHA (1995) *Standard Methods for the Examination of Water and Wastewater*, 19th edn. American Public Health Association, Washington, DC.
- Baker D.B. & Richards R.P. (2003) Phosphorus budgets and riverine phosphorus export in northwestern Ohio watersheds. *Journal of Environmental Quality*, **31**, 96–108.
- Bencala K.E. & Walters R.A. (1983) Simulation of solute transport in a mountain pool-and-riffle stream: a transient storage model. *Water Resources Research*, **19**, 718–724.
- Bernhardt E.S., Hall R.O. & Likens G.E. (2002) Whole-system estimates of nitrification and nitrate uptake in streams of the Hubbard Brook Experimental Forest. *Ecosystems*, **5**, 419–430.
- Bernot M.J. & Dodds W.K. (2005) Nitrogen retention, removal, and saturation in lotic ecosystems. *Ecosystems*, **8**, 442–453.
- Boyer E.W., Goodale C.L., Jaworski N.A. & Howarth R.W. (2002) Anthropogenic nitrogen sources and relationships to riverine nitrogen export in the northeastern USA. *Biogeochemistry*, **57/58**, 137–169.
- Bushong S.J. & Bachmann R.W. (1989) In situ nutrient enrichment experiments with periphyton in agricultural streams. *Hydrobiology*, **178**, 1–10.
- Correl D.L., Jordan T.E. & Weller D.E. (1992) Nutrient flux in a landscape: effects of coastal land use and terrestrial community mosaic on nutrient transport to coastal waters. *Estuaries*, **15**, 431–442.
- David M.B. & Gentry L.E. (2000) Anthropogenic inputs of nitrogen and phosphorus and riverine export for Illinois, USA. *Journal of Environmental Quality*, **29**, 494–508.
- Davis J.C. & Minshall G.W. (1999) Nitrogen and phosphorus uptake in two Idaho (USA) headwater wilderness streams. *Oecologia*, **119**, 247–255.
- Dodds W.K., Evans-White M.A., Gerlanc N.M. *et al.* (2000) Quantification of the nitrogen cycle in a prairie stream. *Ecosystems*, **3**, 574–589.
- Dodds W.K., López A.J., Bowden W.B. *et al.* (2002) N uptake as function of concentration in streams. *Journal of the North American Benthological Society*, **21**, 206–220.
- Downing J.A., Baker J.L., Diaz R.J., Prato T., Rabalais N.N. & Zimmerman R.J. (1999) Gulf of Mexico Hypoxia: Land and Sea Interactions. Council for Agricultural Science and Technology Task Force Report No. 134, Ames, IA.
- Grimm N.B. & Fisher S.G. (1986) Nitrogen limitation in a Sonoran Desert stream. *Journal of the North American Benthological Society*, **5**, 2–15.
- Hall R.O. & Tank J.L. (2003) Ecosystem metabolism controls nitrogen uptake in streams in Grand Teton National Park, Wyoming. *Limnology and Oceanography*, **48**, 1120–1128.
- Hall R.O. & Tank J.L. (2005) Correcting whole-stream estimates of metabolism for groundwater input. *Limnology and Oceanography: Methods*, **3**, 222–229.
- Hall R.O., Bernhardt E.S. & Likens G.E. (2002) Relating nutrient uptake with transient storage in forested mountain streams. *Limnology and Oceanography*, **47**, 255–265.
- Hamilton S.K., Tank J.L., Raikow D.F., Wollheim W.M., Peterson B.J. & Webster J.R. (2001) Nitrogen uptake and transformation in a Midwestern US stream: a stable isotope enrichment study. *Biogeochemistry*, **54**, 297–340.
- Howarth R.W., Billen G., Swaney D. *et al.* (1996) Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: natural and human influences. *Biogeochemistry*, **35**, 75–139.
- Inwood S.E., Tank J.L. & Bernot M.J. (2005) Patterns of denitrification associated with land use in 9 midwestern headwater streams. *Journal of the North American Benthological Society*, **24**, 227–245.
- Jansson M., Andersson R., Berggren H. & Leonardson L. (1994) Denitrification and nitrogen retention in a farmland stream in southern Sweden. *Ambio*, **23**, 326–331.
- Jordan T.E., Correl D.L. & Weller D.E. (1997) Relating nutrient discharges from watersheds to land use and streamflow variability. *Water Resources Research*, **33**, 2579–2590.
- Kemp M.J. & Dodds W.K. (2001) Spatial and temporal patterns of nitrogen in pristine and agriculturally-influenced streams. *Biogeochemistry*, **53**, 125–141.
- Kemp M.J. & Dodds W.K. (2002a) The influence of variable ammonium, nitrate, and oxygen concentrations on uptake, nitrification, and denitrification rates. *Limnology and Oceanography*, **47**, 1380–1393.

- Kemp M.J. & Dodds W.K. (2002b) Comparisons of nitrification and denitrification in pristine and agriculturally-influenced streams. *Ecological Applications*, **12**, 998–1009.
- Marti E., Grimm N.B. & Fisher S.G. (1997) Pre- and post-flood retention efficiency of nitrogen in a Sonoran Desert stream. *Journal of the North American Benthological Society*, **16**, 805–819.
- Marzolf E.R., Mulholland P.J. & Steinman A.D. (1994) Improvements to the diurnal upstream–downstream dissolved-oxygen change technique for determining whole-stream metabolism in small streams. *Canadian Journal of Fisheries and Aquatic Sciences*, **51**, 1591–1599.
- Mason J.W., Wegner G.D., Quinn G.I. & Lange E.L. (1990) Nutrient loss via groundwater discharge from small watersheds in southwestern and south central Wisconsin. *Journal of Soil and Water Conservation*, **45**, 327–331.
- McCutchan J.H., Saunders J.F., Pribyl A.L. & Lewis W.M. (2003) Open-channel estimation of denitrification. *Limnology and Oceanography: Methods*, **1**, 74–81.
- Mulholland P.J., Tank J.L., Sanzone D.M., Wolheim W.M., Peterson B.J., Webster J.R. & Meyer J.L. (2000) Nitrogen processing in a deciduous forest stream: results from a tracer ^{15}N addition experiment in Walker Branch, Tennessee. *Ecological Monographs*, **70**, 471–493.
- Nord E.A. & Lanyon L.E. (2003) Managing material transfer and nutrient flow in an agricultural watershed. *Journal of Environmental Quality*, **32**, 562–570.
- Odum H.T. (1956) Primary production in flowing waters. *Limnology and Oceanography*, **1**, 102–117.
- Payn R.A., Webster J.R., Mulholland P.J., Valett H.M. & Dodds W.K. (2005) Estimation of stream nutrient uptake from nutrient addition experiments. *Limnology and Oceanography: Methods*, **3**, 174–182.
- Peterjohn W.T. & Correl D.L. (1984) Nutrient dynamics in an agricultural watershed: observations on the role of a riparian forest. *Ecology*, **65**, 1466–1475.
- Peterson B.J., Wolheim W.M., Mulholland P.J. *et al.* (2001) Control of nitrogen export from watersheds by headwater streams. *Science*, **292**, 86–90.
- Petry J., Soulsby C., Malcolm I.A. & Youngson A.F. (2002) Hydrological controls on nutrient concentrations and fluxes in agricultural catchments. *The Science of the Total Environment*, **294**, 95–110.
- Rabalais N.N., Turner R.E. & Wiseman W.J. (2002) Gulf of Mexico Hypoxia, a.k.a. 'The Dead Zone'. *Annual Review of Ecology and Systematics*, **33**, 235–263.
- Royer T.V., Tank J.L. & David M.B. (2004) Transport and fate of nitrate in headwater agricultural streams in Illinois. *Journal of Environmental Quality*, **33**, 1296–1304.
- Runkel R.L. (1998) *One-dimensional Transport with Inflow and Storage (OTIS): A Solute Transport Model for Streams and Rivers*. US Geological Survey Water-Resources Investigation Report 98–4018. US Geological Survey, Denver, CO. Available at: <http://co.water.usgs.gov/otis> [last accessed on 12 January 2006].
- Solorzano L. (1969) Determination of ammonium in natural waters by the phenolhypochlorite method. *Limnology and Oceanography*, **14**, 799–801.
- Stream Solute Workshop (1990) Concepts and methods for assessing solute dynamics in stream ecosystems. *Journal of the North American Benthological Society*, **9**, 95–119.
- Tank J.L., Bernot M.J. & Rosi-Marshall E.J. (in press). Nitrogen limitation and uptake. In: *Methods in Stream Ecology* (Eds F.R. Hauer & G.A. Lamberti), Academic Press, New York.
- Tank J.L., Meyer J.L., Sanzone D., Wolheim W.M., Peterson B.J., Webster J.R. & Meyer J.L. (2000) Analysis of nitrogen cycling in a forest stream during autumn using a ^{15}N tracer addition. *Limnology and Oceanography*, **45**, 1013–1029.
- Tilman D., Fargione J., Wolff B., D'Antonio C., Dobson A., Howarth R., Schindler D., Schlesinger W.H., Simberloff D. & Swackhamer D. (2003) Forecasting agriculturally-driven global environmental change. *Science*, **292**, 281–284.
- Townsend A.R., Howarth R.W., Bazzaz F.A. *et al.* (2003) Human health effects of a changing global nitrogen cycle. *Frontiers in Ecology and the Environment*, **1**, 240–246.
- USEPA (1990) Managing nonpoint source pollution: its nature, extent and control. *Water Resources Bulletin*, **21**, 179–184.
- Vanni M.J., Renwick W.H., Headworth J.L., Auch J.D. & Schaus M.H. (2001) Dissolved and particulate nutrient flux from three adjacent agricultural watersheds: a five-year study. *Biogeochemistry*, **54**, 85–114.
- Vitousek P.M., Aber J.D., Howarth R.W., Likens G.E., Matson P.A., Schindler D.W., Schlesinger W.H. & Tilman D.G. (1997) Human alteration of the global nitrogen cycle: sources and consequences. *Ecological Applications*, **7**, 737–750.
- Wanninkhof R., Mulholland P.J. & Elwood J.W. (1990) Gas-exchange rates for a 1st-order stream determined with deliberate and natural tracers. *Water Resources Research*, **26**, 1621–1630.
- Webster J.R. & Ehrman T.P. (1996) Solute dynamics. In: *Methods in Stream Ecology* (Eds F.R. Hauer & G.A. Lamberti), pp. 145–160. Academic Press, San Diego, CA.
- Webster J.R., Mulholland P.J., Tank J.L. *et al.* (2003) Factors affecting ammonium uptake in streams – an

- inter-biome perspective. *Freshwater Biology*, **48**, 1329–1352.
- Wollheim W.M., Peterson B.J., Deegan L.A., Hobbie J.E., Hooker B., Bowden W.B., Edwardson K.J., Arscott D.B., Hershey A.E. & Finlay J. (2001) Influence of stream size on ammonium and suspended particulate nitrogen processing. *Limnology and Oceanography*, **46**, 1–13.
- Young R.J. & Huryn A.D. (1998) Comment: improvements to diurnal upstream to downstream dissolved oxygen change technique for determination of whole-stream metabolism in small streams. *Canadian Journal of Fisheries and Aquatic Sciences*, **55**, 1784–1785.

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